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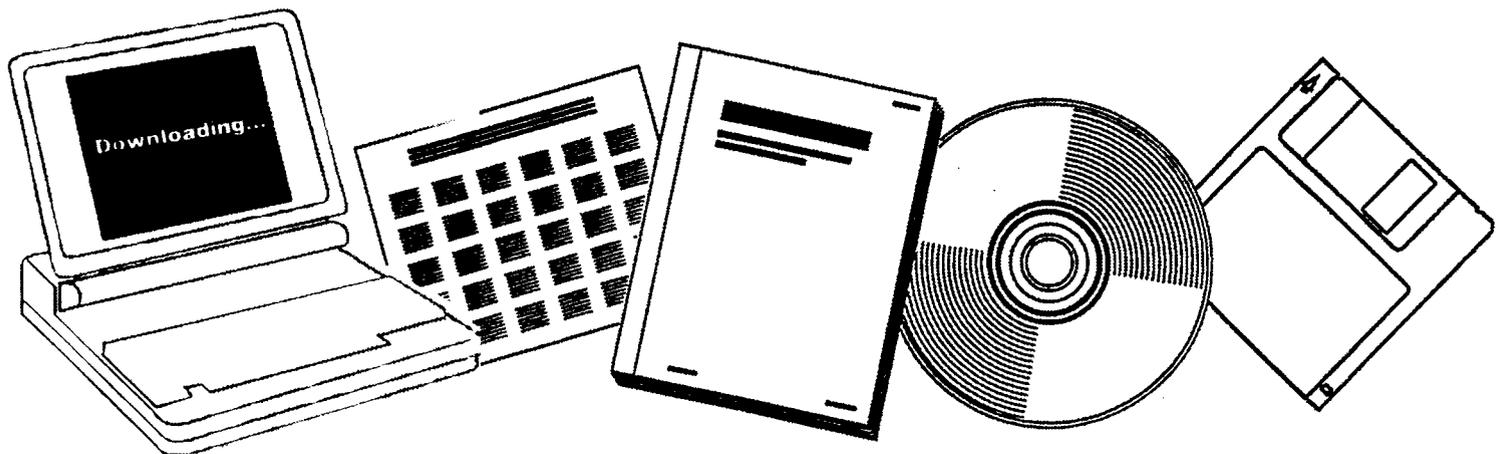
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**EXXON CATALYTIC COAL GASIFICATION PROCESS:
PREDEVELOPMENT PROGRAM. QUARTERLY
TECHNICAL PROGRESS REPORT, JULY
1--SEPTEMBER 30, 1977**

**EXXON RESEARCH AND ENGINEERING CO.
BAYTOWN, TX**

JAN 1978



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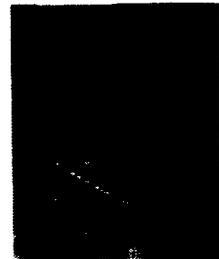
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EXXON CATALYTIC COAL GASIFICATION PROCESS -
PREDEVELOPMENT PROGRAM

Quarterly Technical Progress Report
for the period
July 1 - September 30, 1977

N. C. Nahas - Project Manager

Exxon Research and Engineering Company
Baytown, Texas 77520

January, 1978

PREPARED FOR THE UNITED STATES
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

Contract No. E(49-18)-2369

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ABSTRACT

This report covers the Predevelopment Program activities for the Exxon Catalytic Gasification Process during the period July, 1977 through September, 1977. This work is being performed by the Exxon Research and Engineering Company (ER&E) and is being supported by the United States Energy Research and Development Administration (ERDA) under Contract No. E(49-18)-2369.

The accomplishments during this quarter, summarized by reporting categories, are as follows:

1. Fluid Bed Gasifier Studies

- Operation of the catalyst recovery unit (CRU) continued through July and water soluble potassium was recovered and recycled to the catalyst addition unit (CAU). The recovery of water soluble potassium increased to 94.0%.
- Catalyst recycle operations of the Fluid Bed Gasifier (FBG) were satisfactorily completed in July. Approximately 324 hours of material balanced operation were logged during this period. The recycle catalyst did not show buildup of any inactive species that resulted in loss of catalytic activity.
- The FBG was operated during the first two weeks of August to produce an inventory of char for subsequent catalyst recovery studies. Approximately 134 hours of material balanced operations were logged during the first two weeks of August with good material balance closures. Operations of the FBG as specified in the current contract are now complete and the unit has been shut down.
- Data workup is proceeding on material balances from selected periods of FBG operation.

2. Bench Scale Studies

- Bench scale studies of catalyst recovery via water washing were continued in July. Data were obtained which confirm the discovery in June that exposure of char to air adversely affects catalyst recovery. The effect of residence time on catalyst recovery by water-washing was also investigated. Over the range of conditions investigated, recovery of water-soluble catalyst is independent of residence time.
- Studies continued on the recovery of water insoluble potassium by hydrothermal digestion with calcium hydroxide. The results obtained in laboratory tubing bomb units and in the pilot scale secondary catalyst recovery unit (SCRU) show that thorough rinsing of the digested char can significantly boost recovery. Recoveries in excess of 90% were attained in the SCRU.

- Studies also indicate that temperature, residence time, and calcium loading in the hydrothermal digestion step can be reduced without adversely affecting recovery. Work is continuing to identify the minimum acceptable values for each of these parameters.

3. Engineering Research and Development

- Work has continued on the development of the process basis for the Catalytic Gasification Study Design. The study design will reflect the current concept of a commercial catalytic gasification plant producing approximately 250 MSCF/SD from illinois coal. Preparation of this study design will involve the major share of the engineering effort under the Predevelopment contract during the latter part of the 1977.
- Based on cash flow scoping studies reported in the June Monthly Report, catalyst recovery via hydrothermal treatment with $\text{Ca}(\text{OH})_2$ offers the potential for substantial savings relative to purchased KOH at the market prices. The "minimum cost" of the incremental potassium recovered via this route was estimated to be 36-54% of the cost of purchased KOH, depending on $\text{Ca}(\text{OH})_2$ requirement.

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1. FLUID BED GASIFIER STUDIES (REPORTING CATEGORY 1)

1.1 Fluid Bed Gasifier Operations

Fluid Bed Gasifier (FBG) operations were successfully concluded during the third quarter. The operating history for the last two months of operation is summarized below:

<u>Month</u>	<u>% of Time Onstream</u>	<u>Longest Continuous Run, Hours</u>	<u>Material Balance Closures, %</u>
July	70	290	98-103
August	54	72	98-103

Ten material balance periods occurred during this time and data from these are summarized in Table I.

In July, operations with coal feed impregnated with recycle catalyst solution were successfully completed. During these operations, continued from the previous quarter, recycle catalyst solution was obtained by washing spent gasifier char to recover the water soluble portion of the catalyst. Material balance periods 41-44 summarize the data obtained during catalyst recycle operations this quarter. Gasifier operating conditions were held within narrow limits of target values 1300°F and 100 psia. Carbon and steam conversions remained high during catalyst recycle operations. Carbon conversion was consistently greater than 80 percent and steam conversion varied between 50 and 55 percent. No deleterious effects in FBG operations were observed during catalyst recycle operations. The recycle catalyst did not show buildup of any inactive species that resulted in loss of catalyst activity.

During the remainder of July the unit operated with coal impregnated with fresh catalyst. The synthesis gas flow rate to the unit was increased for balance period 45. Starting with period 46 operation began at high coal and steam feed flow rates one purpose of which was to produce an inventory of gasified char. This char is being used for continuing bench-scale work on catalyst recovery.

Approximately 324 hours of material balanced operation were logged during July. The unit service factor was not as high as the previous month primarily because of several minor mechanical and computer problems.

In the first week of August operations at high feed rates were continued as shown by balance periods 47 and 48. During the second and final week of operations the gasifier bed temperature and feed flow rates were reduced to obtain data useful for development of the reactor model. Balance periods 49 and 50 exemplify operation at these conditions.

Approximately 134 hours of material balanced operations were logged during the two weeks of August. The unit service factor was lower than normal because a feed line plug necessitated bringing the unit down.

Table I

SUMMARY OF FBG MATERIAL BALANCE DATA

	41	42	43*	44*	45	46	47	48*	49	50
Material Balance Period	41	42	43*	44*	45	46	47	48*	49	50
Duration, Hours	24	24	24	24	25	25	24	24	24	24
Catalyst										
% K ₂ CO ₃ on Feed Coal (wt.%)	13	13	14	14	14	15	15	17	15	15
% Na ₂ CO ₃ on Feed Coal (wt.%)	0	0	0	0	0	0	0	0	0	0
Reaction Conditions										
Temperature, °F	1314	1316	1315	1317	1330	1309	1310	1305	1287	1289
Pressure, psig	98.7	98.9	99.0	100.4	99.5	99.2	97.0	100.2	98.7	98.6
Input, lbs/hr (ExN ₂):										
Coal + Catalyst	8.5	9.3	8.6	8.5	7.8	19.7	16.3	15.2	8.9	6.9
Steam	16.0	16.1	15.7	15.6	13.7	24.3	24.3	24.0	14.4	15.0
Syngas	12.3	12.1	12.2	12.8	16.3	13.1	11.8	13.8	14.0	12.7
Total	36.8	37.5	36.5	36.9	37.8	57.1	52.4	53.0	37.3	34.6
Output, lbs/hr (ExN ₂):										
Product gas	26.0	26.6	26.1	25.5	27.0	36.2	35.2	35.1	22.7	22.8
Water	8.3	8.0	8.0	8.3	8.3	12.8	12.3	12.3	10.2	9.4
Carryover	1.1	1.0	1.0	1.2	1.3	3.3	1.4	2.5	1.3	0.7
Withdrawal	2.0	2.3	2.5	2.1	2.2	3.9	3.5	3.6	3.0	1.1
Total	37.4	37.9	37.6	37.1	38.8	56.2	52.4	53.5	37.2	34.0
Accumulation (lbs/hr)	(.60)	.60	(.24)	(.20)	(.45)	(.48)	(.26)	(.60)	(1.05)	.03
Material Balance (%)										
Overall	100.0	102.7	102.4	100.0	101.4	97.6	99.6	99.8	96.9	98.4
Oxygen	100.3	100.0	100.5	97.9	100.2	100.2	102.0	97.3	99.8	100.6
Hydrogen	94.6	95.1	97.0	93.8	98.0	95.2	96.9	98.3	97.2	98.9
Syngas (SCFH)										
CO + H ₂ in Unit	523	520	514	569	609	488	434	457	508	452
CO + H ₂ in Product Gas	561	573	568	553	521	635	646	657	439	462
Syngas Balance (%)	107	110	111	97	86	130	149	141	86	102
Steam Conversion (%)										
By Water Balance	48.8	51.2	49.9	48.0	40.6	48.6	50.4	50.0	30.8	38.1
By Oxygen Balance	49.3	51.1	50.7	44.9	40.9	48.9	53.0	49.0	30.5	39.0
Product gas, Mol % (dry, ExN)										
H ₂	61.4	61.6	62.0	61.7	56.9	54.2	56.1	56.7	58.4	59.4
CO	15.3	14.8	14.5	13.7	15.8	16.9	17.4	17.5	15.4	16.0
CO ₂	14.6	14.7	14.7	14.3	14.8	16.8	16.9	16.6	15.3	15.6
CH ₄	8.0	8.1	7.9	9.5	11.7	10.9	8.6	8.2	11.0	8.2
H ₂ S	0.7	0.8	0.8	0.8	0.8	1.1	1.0	1.0	0.9	0.8
Approach to Methanation Equilibrium, °F	79	81	80	67	31	30	54	70	38	74
Carbon Conversion, %										
By Gas Analysis	87.7	85.3	86.3	84.2	78.5	66.8	79.2	74.4	52.6	73.5
By Solids Analysis	84.5	82.6	83.4	77.3	66.9	71.5	-	76.5	-	-

* Yield Period

Having fulfilled the specifications of the current contract, FBG operations were concluded and the unit was shut down.

1.2 FBG Data Workup

Work is continuing on the analysis of FBG data that has amassed during the past year. Three additional yield periods were designated from FBG material balanced operations from this quarter and are indicated on Table I. This brings the final total of yield periods to 18. Yield periods are chosen on the basis of the quality of the data and the variety of process conditions examined. A full spectrum of solids analyses are being performed on representative samples of feed coal and char collected during each yield period. To date solids data for the first six yield periods are complete and of the remaining 12 all have undergone sieve size analysis and density measurements and about half have been analyzed for their elemental constituents.

Work has also progressed on the off-line material balance computer program. This program uses statistical methods to close all material balances while minimizing the total variance from measured values. Upon completion of yield period analyses the data will be reconciled by this program to determine the most consistent data sets for kinetic and process modeling and for use in commercial design and scaleup.

1.3 Catalyst Recovery Unit Operation

Operation of the Catalyst Recovery Unit (CRU) continued during July and water soluble potassium was recovered and recycled to the Catalyst Addition Unit (CAU). As reported in the July, 1976-June, 1977 Annual Report, operations conducted during the period 6/27 through 7/8 recovered 90.2 percent of the water soluble catalyst. The results of this operations are summarized in Figure 1.

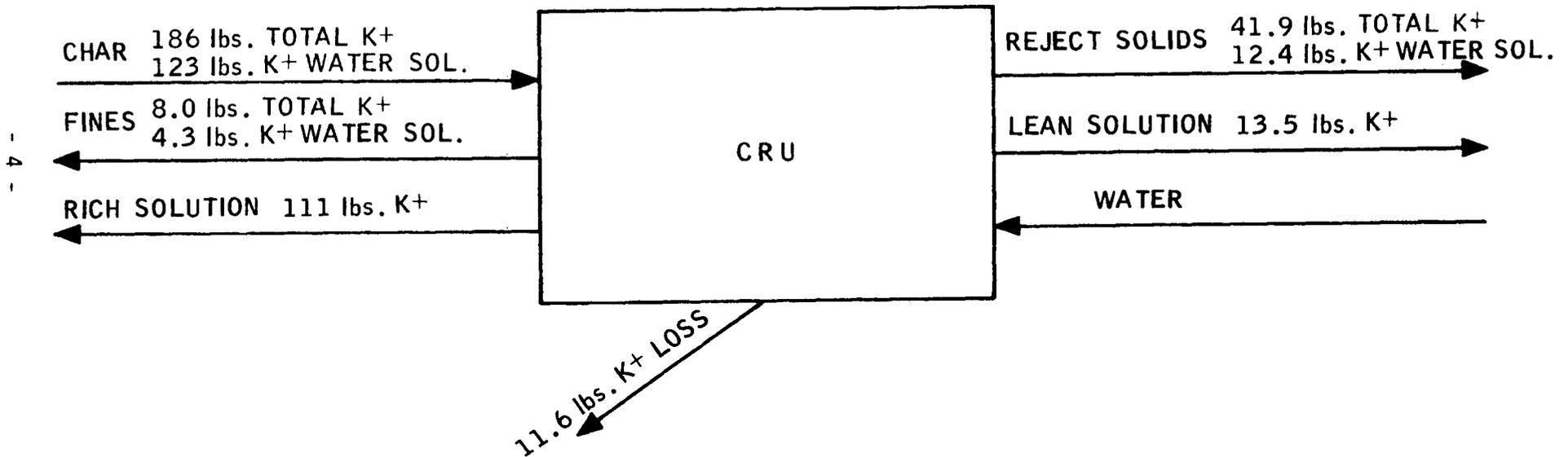
It was subsequently found (see discussion under Reporting Category 2 of this report) that the procedures used to protect the char from air exposure were inadequate and that air exposure reduced recovery. Hence, special char handling procedures were instituted. The N_2 blanketed can of char taken off the gasifier was placed in N_2 filled bags to further protect the char. As an apparent consequence, the recovery of water soluble potassium increased to 94.0% for this second period of operation. Figure 2 gives details of the overall balance for this period.

During the first two operating periods, lime was added to the feed water because there was evidence that some potassium bound to the char at ion exchange sites could be released by calcium ions. When CaO was removed from the water feed during the third operation period, potassium recovery dropped to 89.6% (see Figure 3). This result is consistent with the hypothesis that potassium is tied to char by ion exchange, and that calcium aids in its removal.

FIGURE 1

CATALYST RECOVERY OPERATIONS

PERIOD 1 - OPERATION WITH LIME AND UNBLANKETED CHAR



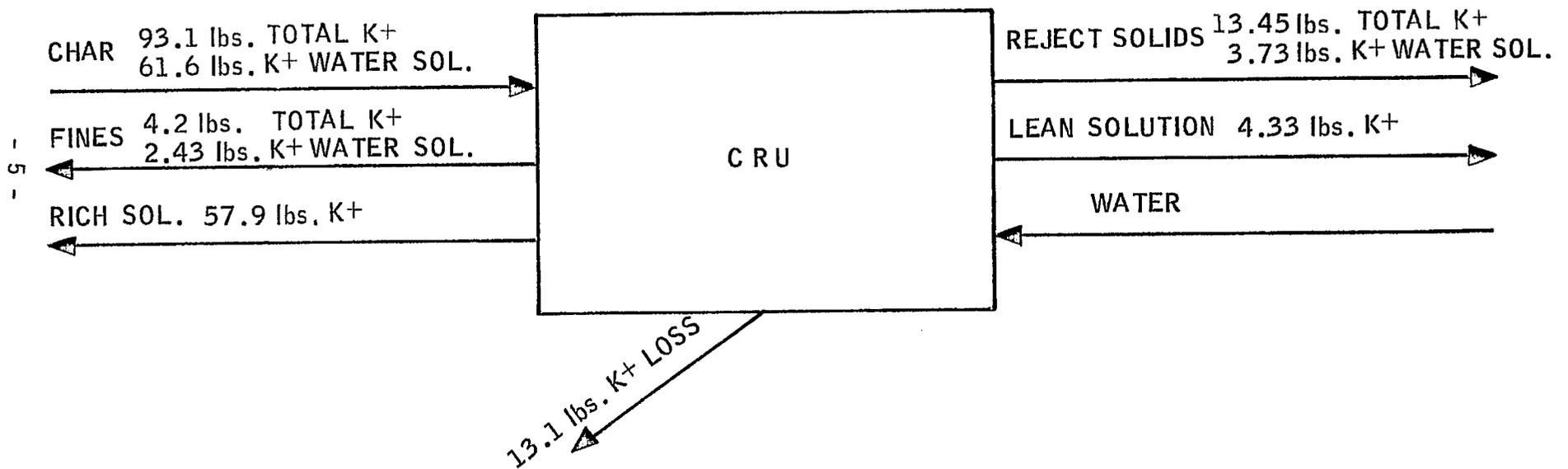
RECOVERY WATER SOLUBLE K+ = $111/123 \times 100\% = 90.2\%$

K+ CLOSURE OUT/IN $\times 100\% = 93.8\%$

FIGURE 2

CATALYST RECOVERY OPERATIONS

PERIOD 2 - OPERATION WITH LIME AND BLANKETED CHAR

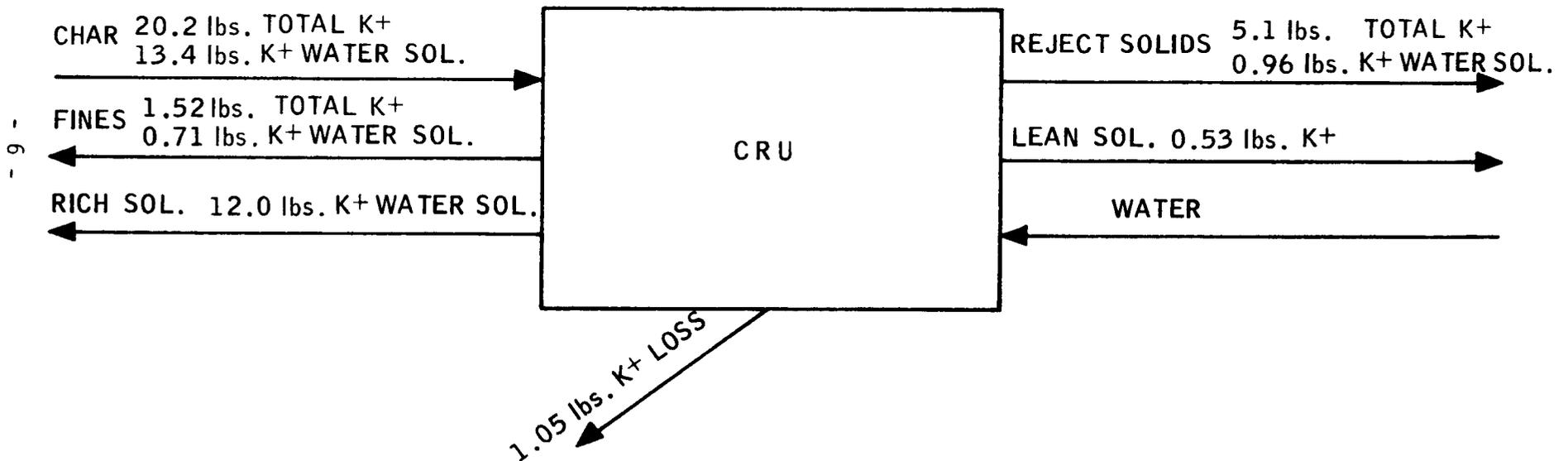


RECOVERY WATER SOLUBLE K+ = $57.9/61.6 \times 100\% = 94.0\%$
K+ CLOSURE OUT/IN $\times 100\% = 85.9\%$

FIGURE 3

CATALYST RECOVERY OPERATIONS

PERIOD 3 - OPERATION WITHOUT LIME AND BLANKETED CHAR



RECOVERY WATER SOLUBLE K+ = $12/13.4 \times 100\% = 89.6\%$

K+ CLOSURE OUT/IN = 94.8%

In summary, these results represent an improvement over previous CRU operations. Increased water rate, introduction of lime into the feed water, and improved procedures for blanketing the char were the factors which apparently account for this improvement.

2. BENCH SCALE STUDIES (REPORTING CATEGORY 2)

2.1 Catalyst Recovery via Water Washing

Bench scale studies of catalyst recovery via water washing were continued in July. Data were obtained which confirm the discovery in June that exposure of char to air adversely affects catalyst recovery and experiments were initiated to determine the mechanism responsible for this behavior. Also, as an input to the Catalytic Gasification Study Design, the effect of residence time on water-soluble catalyst recovery was investigated.

Figure 4 shows all the data obtained to date on the effect of air exposure on potassium recovery, including the data reported in June. These data were obtained by serial washing of FBG char with portions of distilled water. Fresh distilled water was used for each wash (i.e., a cross-current extraction), and the water/char ratio was 3/1 on a weight basis. The newly obtained data for a 24 hour air exposure are most significant since both the location of the recovery curve and its shape are intermediate between the 30 minute and the 3 month curves. This effectively confirms the observation that air exposure reduces recovery, and indicates that the reaction responsible for reduced recovery does not rapidly reach completion, but continues to occur for a period of several hours after initial exposure, if not longer.

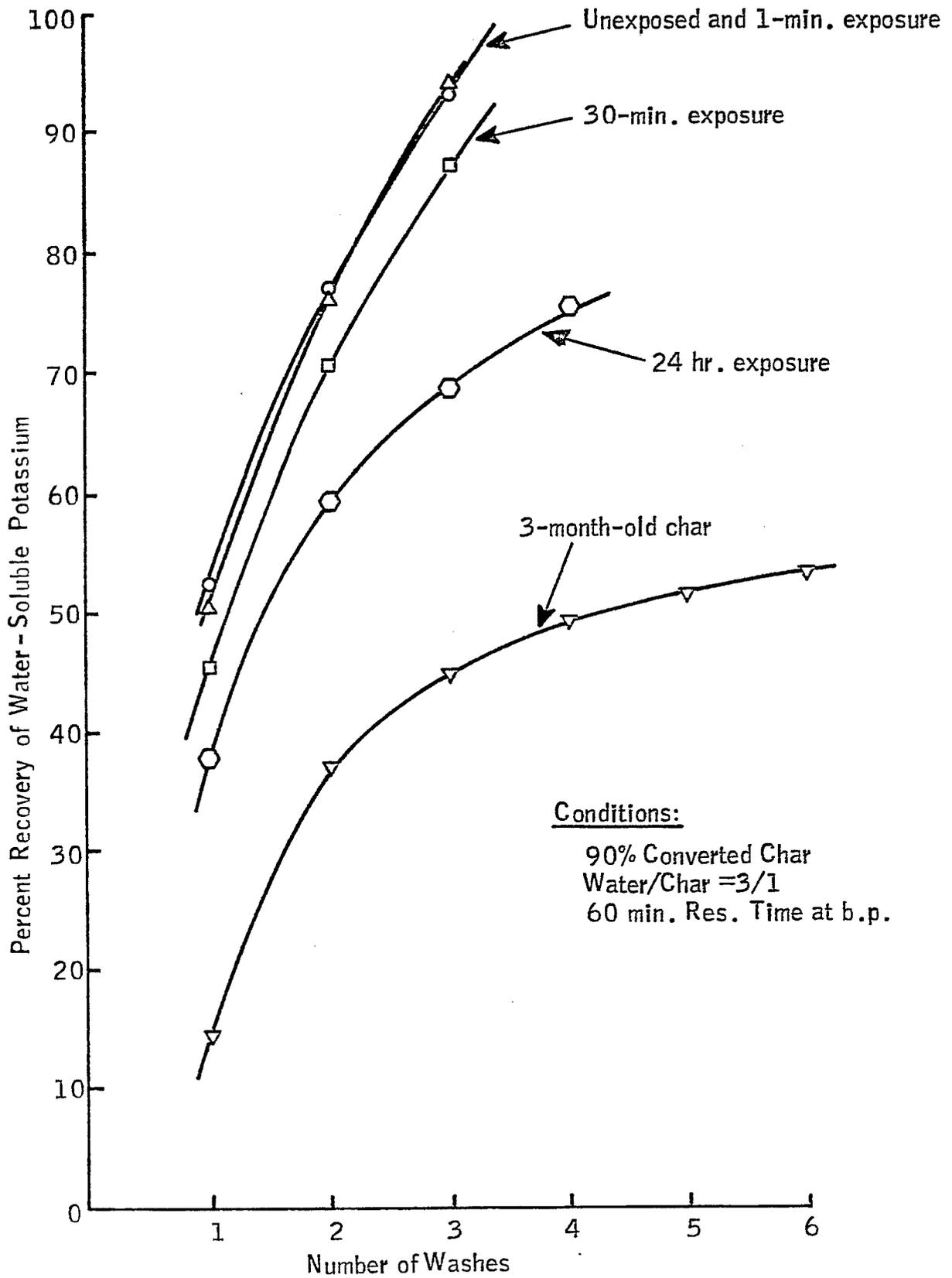
Experiments were initiated to determine the mechanism by which air exposure of char decreases the amount of potassium catalyst which can be recovered by water washing. In order to identify whether the char reacts with oxygen or with water vapor in the air, identical portions of char were exposed to streams of wet air, dry air, wet nitrogen and dry nitrogen for a 24 hour period. At the end of the reaction period, the weight change of each char sample was noted, and two samples of that char were analyzed for water soluble and total potassium. The ratio of water soluble to total potassium was used as an indicator to determine how each gas affects the leachability of the char. The char initially had a water soluble to total potassium ratio of .71. The results of the experiments are as follows:

<u>Reactant Gas</u>	<u>Weight Change</u>	<u>Water Soluble K (% of Total K)</u>
Dry Air	+1%	77
Dry N ₂	0	74
Wet Air	+18	66
Wet N ₂	-	73

The data clearly indicate that there is a reaction between char and wet air, and that this reaction reduces the fraction of potassium which is water-soluble. This supports previous observations in the laboratory that exposure of char to humid air significantly decreases catalyst recovery by cross-current water washing.

FIGURE 4

EFFECT OF AIR EXPOSURE ON POTASSIUM RECOVERY BY WATER WASHING



Any reaction between char and the other gas mixtures, however, is not as obvious. On the basis of the consistently higher ratios of water soluble to total potassium, it appears that char leachability might actually be improved by treatment with the appropriate gases. The usefulness of these data, however, are somewhat limited by the analytical technique used for determination of water soluble potassium. A revised experimental procedure is now being developed, and will be used for further investigation of this behavior.

The effect of residence time on catalyst recovery by water-washing was also investigated. Again, a cross-current extraction was used, with a 4/1 water/char ratio being used for the first wash, and ratios of 3/1 being used for subsequent washes. Inerted char was used in all runs, and the residence times were varied from 5 minutes to 2 hours. The results of these experiments are shown in Figure 5. Over the range of conditions investigated, recovery of water-soluble catalyst is independent of residence time. This result implies that mixing vessels in the catalyst recovery section of the Catalytic Gasification Study Design can be sized to provide good operability, without having to provide extended residence time.

2.2 Recovery of Water Insoluble Catalyst

Bench scale studies continued on the recovery of water insoluble potassium by hydrothermal digestion with calcium hydroxide. The results indicate that more thorough rinsing of the digested char can significantly boost recovery. Also, temperature, residence time, and calcium loading in the digestion step can be reduced without adversely affecting recovery. Parallel studies carried out in the larger Secondary Catalyst Recovery Unit (SCRU) confirmed the results, and demonstrated that thorough washing of the char solids is essential to attaining high recoveries.

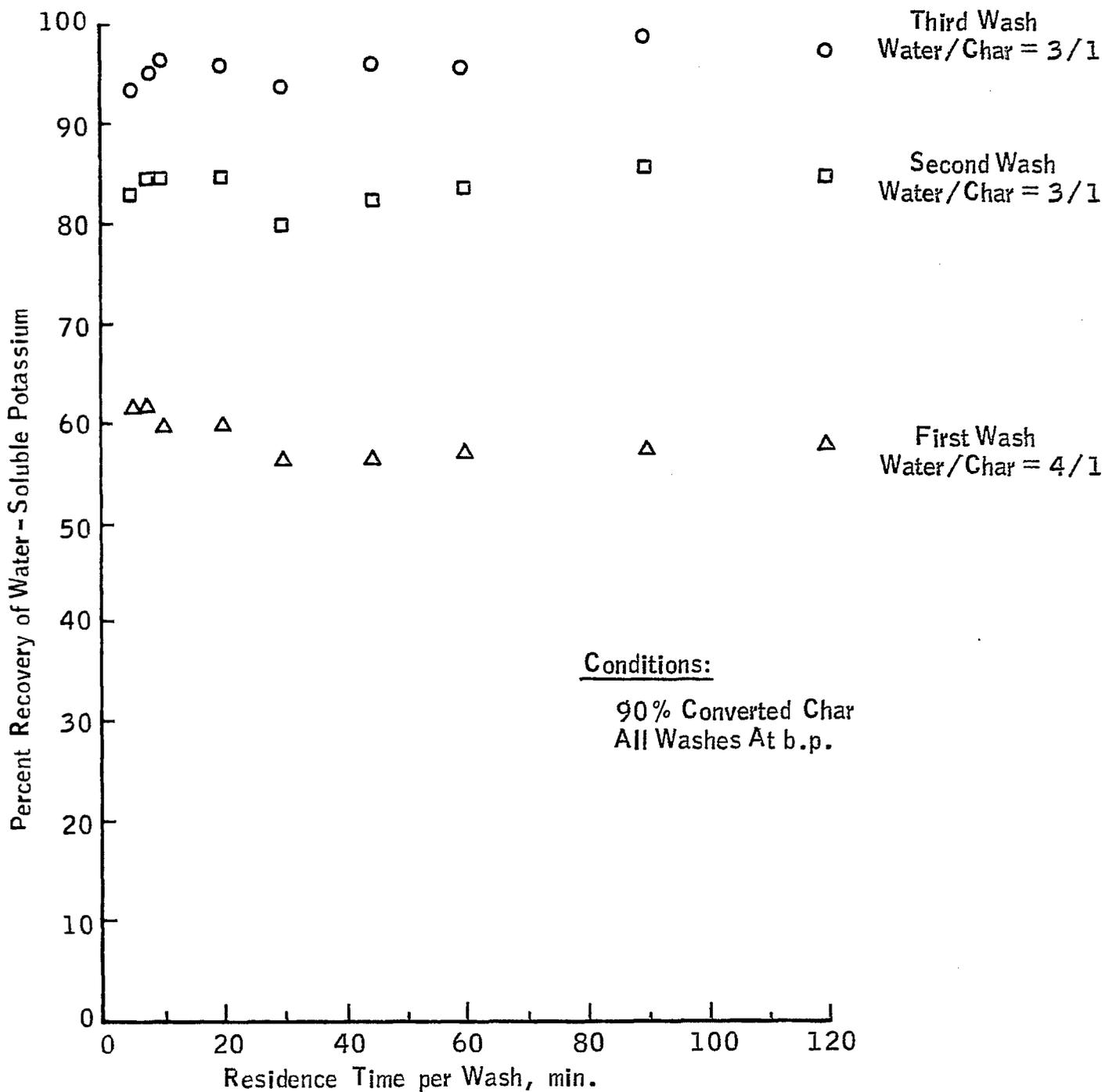
Initial work on the recovery of water insoluble potassium was described in the July 1976-June 1977 Annual Report. The equipment, procedure, and analyses described there were also used for the work described in this report. Since the ultimate recovery of total potassium originally present is the critical parameter in determining the success of a run, experimental results are now reported as percent total potassium removed by the digestion process. Experimentation continued with char produced from coal which contained 15 wt% K_2CO_3 catalyst on the coal.

As described in the Annual Report, the solution used in the digestion process can greatly affect the amount of potassium recovered. Runs made with potassium carbonate and potassium hydroxide solutions showed that much better recoveries of potassium are achieved when the potassium hydroxide solution is used. A 15 wt.% KOH solution was used for most runs made after this determination.

In most of the experiments completed thus far, a liquid to char weight ratio of 10:1 was used. However, in a commercial catalyst recovery system there is an incentive to operate the digestion step with a more concentrated slurry. Therefore, several bench scale runs were made with a liquid:char ratio of 4:1. The runs were made using various amounts of $Ca(OH)_2$ at 400°F for four hours. Recoveries of water-insoluble potassium from un-

Figure 5

EFFECT OF CONTACT TIME ON RECOVERY WITH
LOW WATER/CHAR RATIO



washed char decreased with a decrease in liquid:char ratio as shown in Figure 6. The calcium to potassium mole ratio shown in the X-axis is based on the amount of calcium loaded and the total potassium present on the undigested char fed. The recoveries are based on analyses of the char before and after digestion. The recoveries from these runs may be compared to the recoveries for the runs made with 10:1 15% KOH char which were reported in June, 1977. These data are also shown in Figure 6 for comparison. Several factors could contribute to this decrease in recoveries with a decrease in liquid:char ratio, such as solubility limits or less thorough mixing.

The procedure used for most runs has included rinsing the treated char with an excess of distilled water to remove potassium solution held in the moist char. In order to estimate possible recoveries with minimal water rinsing, the usual procedure was slightly modified for several runs. Temperature and residence time were maintained at 400°F and 4 hours respectively. To avoid the use of excess water, the treated slurry was removed from the tubing bomb and separated by filtration, without adding water, and the filtrate was used to rinse the bomb. The moist char was washed three times with distilled water added at a liquid/char of ~ 3.0. Each wash was held at the boiling point for 15 minutes. This washing procedure is similar to that used to determine the recovery of water soluble potassium by water washing. The data for the runs made with this modified procedure are shown below:

<u>Molar Ratio</u> <u>Ca/K</u>	<u>Total K</u> <u>Recovered</u>
0.85	83%
0.73	87%
0.65	84%
0.48	85%

The recoveries for all of these runs are in the range of 85%, similar to runs made under the same process conditions and washed with an excess of water.

A commercial countercurrent catalyst recovery system would use a KOH/K₂CO₃ solution from downstream water washing steps as a source of liquid for the digestion process. For this reason, an attempt was made to simulate the recycle of solution to the digestion process on the bench scale. Portions of solutions resulting from runs made with 15% KOH were concentrated and used instead of 15% KOH for the first recycle runs. The recycle solutions were made up to contain an amount of potassium equivalent to the amount which would be found in a equal volume of 15% KOH. The solutions resulting from runs were subsequently reused through two or three cycles as shown by the flow diagram presented in Figure 7. The data from two series of runs conducted with 4:1 liquid:char ratios are shown below:

FIGURE 6

EFFECT OF SLURRY CONCENTRATION
ON POTASSIUM RECOVERY

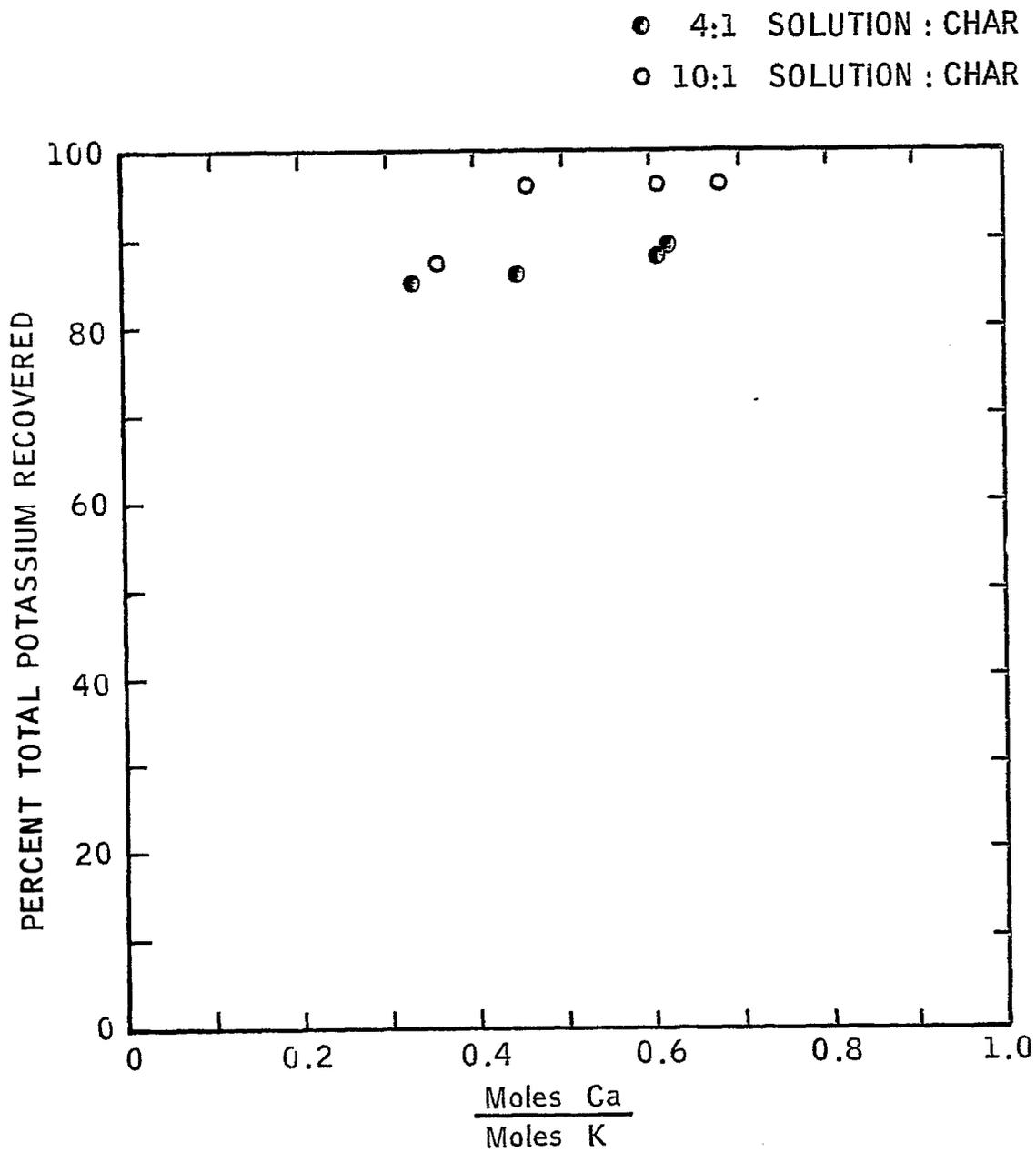
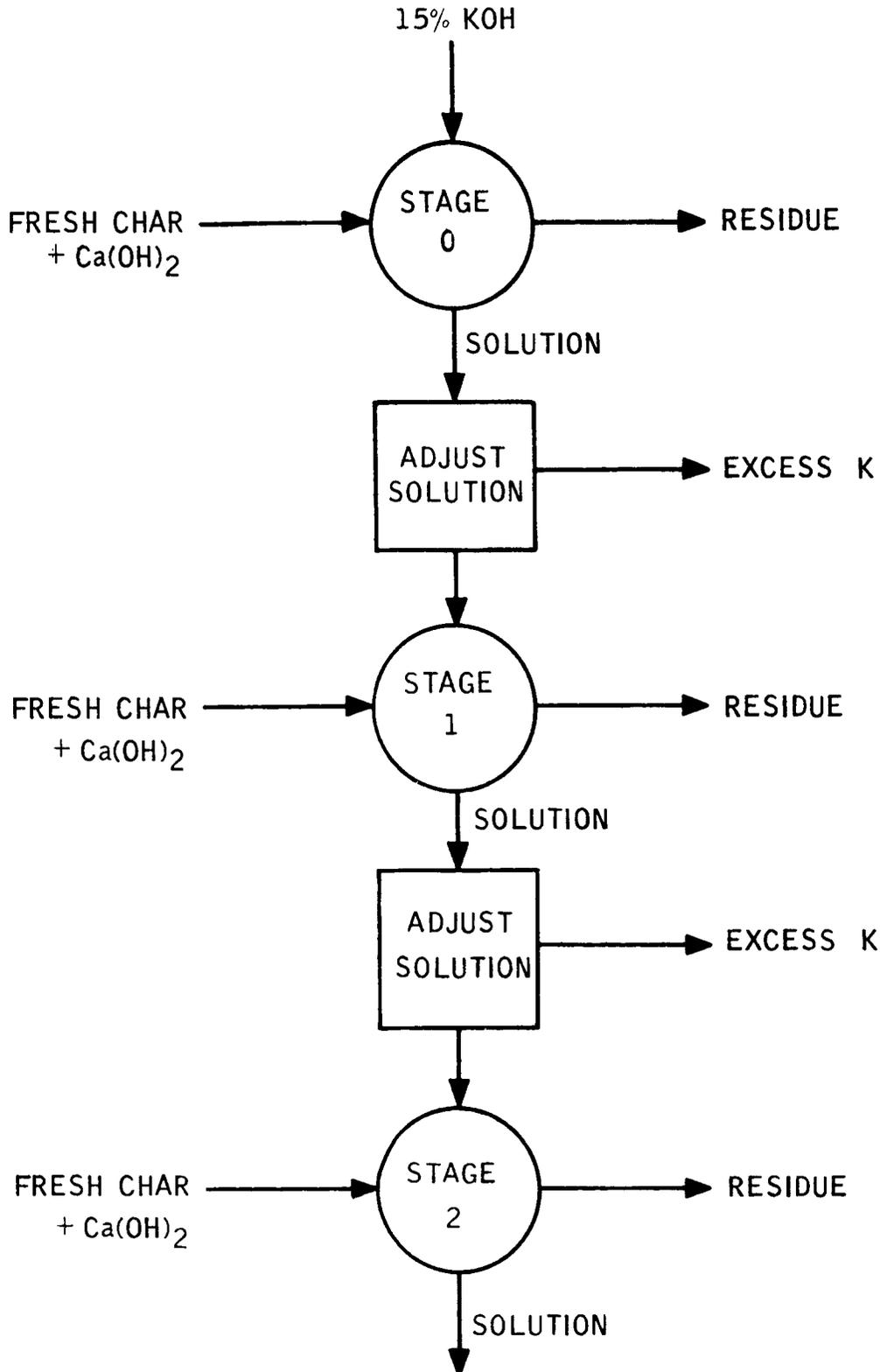


FIGURE 7

SIMULATION OF DIGESTION WITH DOWNSTREAM
SOLUTION COMPOSITIONS



<u>Ca/K</u>	<u>Cycle No</u>	<u>Total K Recovered</u>
0.62	0	89%
0.68	1	88%
0.62	2	85%
0.62	3	85%
0.61	0	88%
0.65	1	87%
0.61	2	85%

Recoveries from these recycle runs are in the same range as recoveries obtained in runs made under the same conditions with fresh 15% KOH solution. These results indicate that the results obtained with KOH solution are representative of what should be achieved with a recycle solution in the commercial countercurrent process.

A series of experiments to investigate the effect of temperature on potassium recoveries was initiated in August. The runs were made with the usual procedure, including an excess of water to rinse the treated char. Recent work has indicated that acceptable recoveries may be possible at a temperature as low as 300°F with 4 hours residence time. These data are summarized below:

<u>Run Temperature</u>	<u>Molar Ratio Ca/K</u>	<u>Total K Recovered</u>
200°F	0.78	74%
300°F	0.81	87%
350°F	0.80	86%
400°F	0.68	89%
450°F	0.84	90%

Several experiments were made to investigate the effect of residence time on potassium recoveries. Runs were made at 300°F and several residence times. The results from these runs are summarized below:

<u>Residence Time</u>	<u>Mole Ratio Ca/K</u>	<u>Total K Recovered</u>
2 hours	0.63	82%
3 hours	0.67	86%
4 hours	0.81	87%
5 hours	0.66	86%

These data show that essentially the same potassium recovery was achieved at residence times 3, 4, and 5 hours. Therefore, a 3 hour residence time may be adequate for the digestion reaction. Also, on the bench scale, part of the residence time is required to heat the contents of the tubing bomb to the required temperature. In a commercial process, this heatup

time would be minimized, and a residence time of less than 3 hours might be adequate.

A series of experiments to investigate the effect of calcium loading on potassium recoveries was initiated in September. Several runs were made at 400°F and 4 hours, and are summarized below:

<u>Mole Ratio</u> <u>Ca/K</u>	<u>Total K</u> <u>Recovered</u>
0	71%
0.29	74%
0.49	79%
0.68	89%
0.87	82%
1.04	90%

From these data, a stoichiometric Ca/K ratio of 0.7-0.8 appears to be the minimum necessary for good potassium recoveries.

Additional studies were carried out in the pilot-scale Secondary Catalyst Recovery Unit (SCRU). This unit, constructed in July, consists of a digester, a pressure vessel with a capacity of approximately 100 gallons which operates at 400°F and 250 psi. It is equipped with an impeller for agitation, and an internal steam/water coil for rapid heatup and cool down during startup and shutdown. Electrical resistance heaters supply additional heat. The slurry product from the digester is fed to a batch vacuum filter where liquids are separated from the solids. The resulting solutions and solids are weighed and analyzed for their potassium content.

The procedure used in runs in the SCRU was similar to that used in bench scale work. Process solution, either water or KOH solution, was pumped into the digester and mixed with calcium hydroxide. Char was then added, and the mixture was heated and agitated for the reaction period. At the end of the reaction period, the slurry was filtered to separate liquids and solids.

Washing of the digested char had a significant effect on results. As in the bench scale work, the digested solids were reslurried with fresh water to wash solubilized potassium from the pores. However, in the larger SCRU equipment, more complete washing of the solids is possible because the digested char samples, typically more than 100 lbs, can be reslurried prior to each wash step without appreciable handling losses. As a result, potassium recoveries in excess of 90 percent were obtained after five cross-current washes of the digested char.

The results of the SCRU runs are summarized in Table II. Recoveries after three washes are approximately the same as recoveries obtained under similar conditions in bench scale experiments. The extra recovery obtained after additional washes emphasizes the importance of thorough washing.

Table II

RECOVERY OF POTASSIUM CATALYST BY HYDROTHERMAL
DIGESTION WITH $\text{Ca}(\text{OH})_2$ IN SCRUBBER

Run No.	Conditions				Cumulative Percent Potassium Recovered in Solution						
	Reaction Time(hrs)	Temp. (°F)	$\frac{\text{Moles Ca}}{\text{Moles K}^{(a)}}$	Solution lbs/lb char	Digestion Step	First Wash	Second Wash	Third Wash	Fourth Wash	Fifth Wash	Sixth Wash
2	4	400	0.61	3 lb H ₂ O	30.2						
3	4	400	0.00	3 lb H ₂ O	27.4	47.0	52.2				
4	4	400	0.60	4 lb H ₂ O	36.5	77.2	84.9	88.2			
5	4	400	0.39	4 lb 8.79% K	-84.4 ^(b)	47.4	71.9	76.7	81.2	83.4	
6	4	400	0.37	4 lb 9.34% K	-21.9	62.9	77.9	82.5	84.7		
7	4	400	0.57	4 lb 4.57% K	- 0.7	50.1	75.3	81.2	84.1	85.1	
8	4	400	0.89	3 lb H ₂ O	46.4	71.7	82.1	87.5	90.7	92.0	
9	2	300	0.81	4.6 lb 8.9% K	-60.1	51.4	71.2	83.2	89.0	93.5	96.0

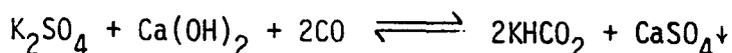
(a) Ca:K ratio based upon potassium in char

(b) Negative recoveries indicate holdup of KOH solution on char

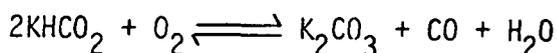
Future studies on recovery of insoluble catalyst will continue to examine the effects of calcium loading, residence time, and temperature in order to identify the minimum values necessary to achieve high recoveries.

2.3 Catalyst Recovery via the Formate Process

Investigations were initiated into the use of the formate process for recovery of water insoluble catalyst. Originally developed for the manufacture of potassium carbonate, the formate process involves the reaction of potassium sulfate with lime and carbon monoxide at 200°C and 440-470 psi, according to the equation:



In the original process, this was followed by a calcining reaction to convert the formate to carbonate:



For enhanced catalyst recovery, insoluble potassium is substituted for sulfate in the formate reaction, and the calcining reaction is not necessary since potassium formate is believed to be equivalent to potassium carbonate as a gasification catalyst.

The formate process has some potential advantages over the hydrothermal process for recovery of water insoluble potassium. By the conversion of lime to calcium formate considerably more calcium is solubilized thereby providing a greater driving force for reaction. Also, any sulfate present on the char is converted to catalytically active potassium formate. A third possible benefit is that makeup potassium in the form of sulfate could be added directly to the char slurry, eliminating the need for separate catalyst manufacture facilities.

As a preliminary test of the viability of the formate process for enhanced recovery, a series of tubing bomb experiments were conducted in which FBG char, water, calcium hydroxide and carbon monoxide were reacted for 3 hours at 200°C. The initial bomb pressure was 450 psig, but the pressure dropped as CO was consumed by reaction. At the end of the reaction period, the mixture was rapidly cooled and the solid residue separated by filtration. The solids were then water washed twice and potassium recovery calculated using analyses of the recovered liquid and the starting char material. The results are as follows:

Ca/K Insol (Mol/Mol)	Initial Charge to Bomb			Recovery of Total K (%)
	Total K (Millimoles)	Ca(OH) ₂ (Millimoles)	CO (Millimoles)	
0.6	85	27	41	63
1.3	85	54	41	85
2.6	85	108	41	74
3.9	85	162	29	85

Clearly, the formate reaction results in total potassium recoveries significantly in excess of those attainable by water washing alone. However, in these preliminary runs, the potassium recoveries are not any greater than those attained in hydrothermal treatment. The formate process still has the advantage of converting sulfate to formate, a feature not shared by the hydrothermal process. As a test of this reaction, several additional tubing bomb runs were conducted using the procedure outlined above, with potassium sulfate being used as the potassium source. Pressure above the reaction mixture was monitored to follow the course of the reaction, and the reaction was judged complete when the pressure fell to the vapor pressure of water at 200°C, about 240 psi. The results show that CO uptake occurs readily, driving the reaction to completion in a relatively short time.

<u>K₂SO₄</u> <u>(Millimoles)</u>	<u>Initial Charge to Bomb</u>			<u>Time Required</u> <u>For all CO to</u> <u>be Consumed, min.</u>
	<u>Ca(OH)₂</u> <u>(Millimoles)</u>	<u>CO</u> <u>(Millimoles)</u>	<u>H₂O</u> <u>(Ml)</u>	
29	54	40	30	110
29	27	40	30	110
47	108	29	60	50
29	27	29	60	60

Future investigations of the formate process will be carried out in a stirred autoclave with constant CO pressure over the solution, providing a closer approximation to potential commercial conditions.

3. ENGINEERING RESEARCH AND DEVELOPMENT (REPORTING CATEGORY 3)

3.1 Catalytic Coal Gasification Commercial Plant Study Design

Work continued through the third quarter of 1977 on the development of the process bases and heat and material balances for the Catalytic Coal Gasification Commercial Plant Study Design. The Study Design will reflect the current conception of a commercial catalytic gasification plant producing approximately 250 MSCF/SD of SNG from Illinois coal. Estimates will be made of both investment and operating costs. Preparation of this Study Design will involve the major share of the engineering effort under the Predevelopment Program during the second half of 1977.

The first major step in the Study Design effort is developing the process basis for the catalytic gasifiers, recycle synthesis gas loop, and catalyst loop. Information from several sources was gathered and reviewed as part of the basis-setting effort. Laboratory data generated during the current program were reviewed to determine their impact on the Study Design. Consulting experts in specialized areas of engineering technology have contributed studies and recommendations on critical plant areas. Work done under the separate contract on "Scale-Up Requirements of the Exxon Catalytic Coal Gasification Process" (ERDA Contract No. EX-76-C-01-2480) has been reviewed to incorporate applicable technical findings.

The gasifier pressure for the new Study Design was set at 500 psia, the same pressure as in previous studies. Based on engineering work carried out in the first half of 1977, the gasifier temperature was reduced from 1300°F to 1275°F to take partial advantage of savings indicated for lower temperature operation. Although still lower temperatures could lead to additional savings, designing for a temperature below 1275°F at this time is judged to involve too great an extrapolation from the current data base obtained in Fluid Bed Gasifier (FBG) operations. Most FBG material balance periods have been carried out at about 1300°F.

Key inputs to the gasifier heat balance were provided by studies of coal feeding methods and gasifier lining design. The first study concluded that the coal feed injection method which appears to have the best chance of technical success is dense-phase pneumatic conveying upward through the gasifier bottom head in multiple feed lines. This approach is expected to provide very good mixing of the feed coal with the char in the gasifier fluid bed. Thus, dense bottom injection is judged less likely to lead to stagnation than the alternatives of dilute-phase conveying or side injection. In addition, dense conveying requires less injection gas than dilute conveying. The injection gas must bypass the steam/recycle preheat furnaces. The dense-phase approach allows the preheat furnace coil outlet temperature to be lowered by about 70°F relative to the dilute-phase approach, since more gas passes through the furnaces to carry heat into the gasifiers. Thus, there is a significant reduction in furnace investment with the dense-phase approach. The second study, on gasifier lining design and resultant heat losses to the environment, is still in progress.

Data from FBG material balance periods were reviewed to develop bases for gasifier fines carryover and gasifier char withdrawal rates and properties. These bases are being used to design solids recovery equipment for the gasifier effluent gas stream and to design the catalyst recovery system. Data on properties of the "mid-char" from the FBG fluid bed were also reviewed to set part of the basis for gasifier volume calculations using the catalytic gasifier reactor model.

In other work associated with the Study Design, a flow sequence for the gasifier effluent solids recovery and heat recovery train has been defined. Work is underway to estimate the chemistry and heats of reaction of catalyst reactions in the gasifiers, so that a final heat and material balance for the gasifiers and recycle synthesis gas loop can be completed.

Screening studies of acid gas (CO_2 and H_2S) removal alternatives to select one for use in the Study Design have also begun. The three alternatives being evaluated at this time are selective refrigerated methanol scrubbing, selective scrubbing with a heavy glycol, and non-selective hot potassium carbonate scrubbing. Selective processes recover essentially all the H_2S from the gasifier effluent in one H_2S -rich stream, and most of the CO_2 in a second stream. Non-selective processes recover H_2S and CO_2 together in a single stream. Costs for conversion of the H_2S to by-product elemental sulfur are significantly less with selective processes. For this reason, the impact of each acid gas removal alternative on the costs of sulfur recovery will also be reflected. Vendors have been contacted to provide design and cost information on the first two scrubbing alternatives. Equipment for the third alternative, hot potassium carbonate scrubbing, will be sized and cost-estimated based on commercial experience.

Upon completion of the process bases and heat and material balances, equipment specifications lists will be prepared for all onsites process sections. Overall plant balances will be finalized for steam, electric power, and other utilities, and equipment lists will be compiled for all required utilities and general offsites facilities. The total capital investment for the plant will be estimated. Operating costs and overall product cost will also be estimated.

3.2 Catalyst Recovery Studies: Screening Study of $\text{Ca}(\text{OH})_2$ Digestion

Based on the results of cash flow scoping studies carried out in the second quarter of 1977, catalyst recovery from spent gasifier char and fines via digestion with $\text{Ca}(\text{OH})_2$ offers the potential for substantial savings relative to purchased KOH at the market price. The operating cost for the incremental potassium recovered via this route was estimated to be 36-54% of the cost of purchased KOH, depending on the $\text{Ca}(\text{OH})_2$ requirement. This evaluation was based on early bench-scale experiments. Although investment charges for the digestion step were not included in the operating cost, the added investment required for these facilities is expected to be small.

A screening study was begun in July, 1977 to define the facilities and quantify the investment required for catalyst recovery via this method.

The objective was to compare the investment and operating costs for this case with costs for water washing alone to select the preferred catalyst recovery system for inclusion in the Study Design.

The process basis for this screening study was set in August based on the available laboratory data on calcium hydroxide digestion and water-washing. The important basis items selected for the screening study are summarized below:

- Feed catalyst loading is 15% K_2CO_3 -equivalent on dry coal
- 27% of this total potassium ties up with the coal ash as water-insoluble $KAlSiO_4$, and thus only 73% of the feed potassium can be recovered by water washing alone.
- In contrast, after digestion 90% of the potassium fed to catalyst recovery is water-soluble and thus recoverable.
- The digestion step replaces one stage of the water-wash sequence. Based on available bench lab results, the operating conditions for the digestion vessels are 250 psia, 400°F, 4 hours residence time, and a lime (CaO) rate which reflects a molar ratio of calcium to the total potassium feed of 0.6/1. (CaO hydrolyzes to $Ca(OH)_2$ in aqueous solution.)
- The makeup catalyst (30% KOH solution) is added to the digestion step to take advantage of probable enhanced recovery at higher pH.
- The recovered rich catalyst solution is stripped with CO_2 before returning to the catalyst addition facilities in order to minimize recycle of K_2S , which may oxidize to catalytically less active K_2SO_4 in the catalyst addition step.
- The forms of water soluble potassium in the stripped rich catalyst solution are mostly K_2CO_3 and $KHCO_3$, with about 1% each of K_2S , K_2SO_4 , and $K_2S_2O_3$.

Using this process basis, equipment lists were prepared for the facilities required and were submitted for cost estimating early in September.

Based on the results of experiments in progress in September, it appeared that the process basis set for the screening study was too conservative with regard to the digestion pressure and residence time required to obtain 90% recovery of the total potassium fed. So that the screening study could fully reflect the results of the continuing experiments to define the actual process requirements for $Ca(OH)_2$ digestion, development of economics was deferred until the latter part of the fourth quarter. Based on the favorable results obtained in the earlier cash flow studies, $Ca(OH)_2$ digestion will be included in the catalyst recovery processing for the current Study Design. A revised process basis will be used for the Study Design system based on the latest laboratory results.

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